Timing of interfacial diffusion and (stereo)crystallization to tailor mechanical properties of additively manufactured poly(lactides)

Summary

Additive manufacturing, more commonly known as 3D printing, is a technology that has developed rapidly as a niche within the field of discrete manufacturing. It provides an avenue to manufacture unique products of high added value that rely on customization and nearly endless design flexibility. We see examples being progressively introduced in several industries like automotive, aerospace, art and medical. Nevertheless, despite successes with materials like metals, ceramics and living materials, a mismatch in product quality and expectations has been restrictive in the mass adoption of thermoplastics in 3D printing.

Fused deposition modeling (FDM) is by far the most popular 3D printing technology for thermoplastics due to ease of operation, low cost and availability of a variety of materials. It is an extrusion-based technique in which thermoplastics are molten at elevated temperatures and deposited, i.e., welded with high spatial control to form layer-by-layer the desired product. In comparison to other successful construction materials such as metals, polymer molecules are based on long arrays of covalently bound monomeric building blocks. The consequential entanglements between polymer molecules are the origin of the praised mechanical properties accessible via mild melt-based processing conditions, but tremendously reduce the timescales of filament fusion, molecular mixing and crystallization. The aim of this thesis is to generate a fundamental understanding of the physical processes underlying weld formation, assisting in optimum inter-layer mechanical properties in additive manufacturing. Tailoring the molecular design of polymers enables the alignment of timescales of molecular and structural processes with those of this additive manufacturing technology.

To realize stable, durable and high product performance of fused deposition modeled parts, the effect of molecular design parameters and process specific heat fluctuations on structure and morphology is studied in ***Chapter 2***. By selection of poly(lactides) with systematic variations in molar mass and L-enantiomeric purity, molecular and crystallization dynamics are controlled and correlated to (i) print resolution, (ii) mechanically effective bonding via macroscopic fusion and successive molecular diffusion, and (iii) thermodynamic stability. Macroscopic fusion during melt deposition is governed by molecular dynamics of solidification and is positively affected by low print speed and low molar mass. However, low molar mass and high L-enantiomeric purity induce melt crystallization during deposition, limiting interfacial molecular diffusion. By increasing molar mass, crystallization during melt deposition suppresses, facilitating interfacial molecular diffusion that promotes the formation of mechanically effective interfaces. Additionally, structure evolution primarily occurs via cold crystallization in successive annealing

cycles. Layer-by-layer deposition induces spatial variations in crystallinity and thus thermodynamic instability. These findings highlight that optimum macroscopic mechanics and geometrical stability of fused deposition modeled poly(lactide) parts are compromised and require judicious timing of crystallization and molecular diffusion.

To promote molecular diffusion and/or crystallization at fused deposition modeled weld interfaces, the addition of chemically identical low molar mass fractions to high molar mass PLLA is discussed in ***Chapter 3***. The enantiomeric composition of the low molecular weight fraction is either random (PDLLA) or opposite, promoting molecular diffusion or stereocomplex nucleation respectively. By employing torsional dynamic mechanical analysis, calorimetry and rheology, it is seen that the low molecular weight additives of random L and D enantiomeric composition promote molecular diffusion across the weld interfaces. Nevertheless, the low amount of new entanglements formed upon interfacial mixing and incomplete crystallization induce poor interfacial stiffening and reduced thermodynamic stability. Poly(lactide) stereocomplex enriched interfaces promote crystallization during interfacial mixing, but the hindered diffusion restricted by crystallization at the interface limits molecular mixing and thus the extent of mechanical stiffening. Ultimately, combining melt plasticization and increased crystallization rate by stereocomplex based additives distinctly increases weld stiffness and provides thermodynamic/geometrical stability.

In ***Chapter 4***, a novel route to improve the interlayer weld stiffness is proposed by the timing and spatial direction of poly(lactide) stereocrystallization across fused deposition modeled interfaces. Stereocrystallization in poly(lactides) occurs upon molecular mixing of enantiomerically opposite polymers in the melt state. The resulting stereocrystals possess a melting temperature of approximately 50 to 60°C higher than the so-called homocrystals. Per definition, stereocrystals involve two enantiomerically opposite poly(lactide) chains and are hypothesized to physio-mechanically interlock the weld interfaces. Fundamental insight in the kinetics and spatial evolution of interfacial stereocrystallization is studied by rheometry and synchrotron wide angle X-ray diffraction tomography. By alternating deposition of enantiomerically opposite poly(lactides) via a twin nozzle setup, the concept of interfacial stereocrystallization is demonstrated in fused deposition modeling. The printed samples are morphologically and thermomechanically studied by polarized optical microscopy, FTIR microscopy and dynamic mechanical analysis. FTIR microscopy reveals that interfacial diffusion of polymers during fused deposition modeling occurs. The net local heat dosage, which depends on print speed, governs the length-scales of stereocomplexation and thus mechanical reinforcement. Interfacial stereocomplexation of poly(lactides) in FDM leads to a distinct 40% increase in stiffness and nucleation of bulk filaments, aiding in thermodynamic and geometrical stability.

Chapter 5 addresses the effect of temperature and relative molar masses in interfacial stereocomplexation of heterogeneous poly(lactide) melts. Rheometry, differential scanning calorimetry and FTIR imaging reveal that a transition from high to low stereocrystallization rate is dictated by a critical network density that impedes diffusion and crystal growth. If the initial relative viscosity is low (affected by temperature and relative molar mass), the time to reach the critical network density is high as a higher number of stereocrystals per chain is demanded in critical network formation. Consequently, the length-scales of stereocrystallization and ultimate mechanical stiffening are high. The relationship reverses in case of a relatively high initial viscosity. The fundamental understanding of the timescales of interfacial diffusion, successive stereocrystallization and nucleation of homocrystallization upon further cooling, assists in the technical realization of mechanically reinforced polymer-polymer interfaces.

In ***Chapter 6,*** the future perspectives of this research are explored for the manufacturing and biomedical applications. In the context of biomedical applications, a potential area of future research for tissue engineering is presented whereby spatially directed stiffness in FDM parts is introduced to direct preferential stem cell differentiation in tissue regeneration.